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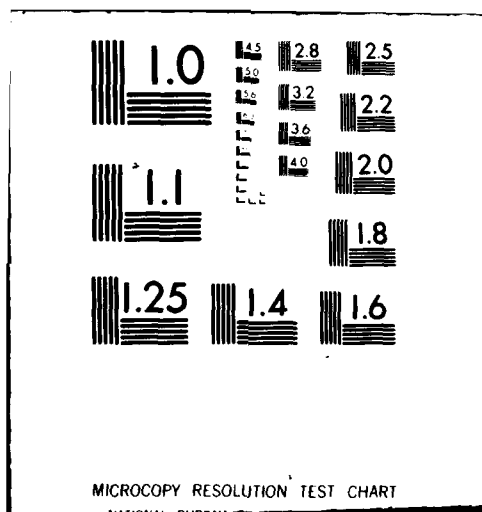
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Studies resulted in the first direct proof of chain transfer to solvent in the cationic polymerization of vinyl ethers by both chemical initiation and initiation using radiation. It was shown that incomplete dissociation of the initiator salt can influence the rate constant for polymerization by a factor of three or more. It was discovered that solvent effects can have remarkable effects upon the rate of polymerization. For example it was found that a linear relationship exists between the logarithms of the rate constants and the reciprocals of the dielectric constants. Results indicate that there is little or no solvation of the propagating		

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20. species by monomer. In certain circumstances there could be a self-solvation of the propagating cations by their own chains. Progress on the radiation chemistry work on polyphosphazenes has moved slowly due to complicating factors caused by the broad and sometimes bimodal nature of the molecular weight distributions.



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FUNDAMENTAL INVESTIGATIONS

IN

POLYMER CHEMISTRY

FINAL REPORT

Vivian T. Stannett
David R. Squire

U. S. Army Research Office

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29 June 1975 - 31 March 1982

North Carolina State University
Raleigh, North Carolina

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FUNDAMENTAL INVESTIGATIONS IN POLYMER CHEMISTRY

FINAL REPORT*

Throughout the years of this research project, an underlying theme has been the comparison of the kinetics and of the stereochemistry of polymerization of vinyl ether monomers in solution via chemical initiation versus radiation initiation. Our studies resulted in the first direct proof of chain transfer to solvent in the cationic polymerization of vinyl ethers by chemical initiation in methylene chloride and by initiation using radiation. These results showed that for chemical initiation in the cationic polymerization of vinyl ethers, the incomplete dissociation of the initiator salt can influence the rate constant for polymerization by as much as a factor of three or more. This work brought the cationic rate constants for polymerization into rather close agreement with those determined using radiation for several vinyl ethers. However, the work also surfaced a number of mysteries which in some cases we are still trying to unravel. For example, we have for the first time measured the cationic rate of polymerization, activation energy, and heat of polymerization of isopropyl vinyl ether using a chemical initiator. Interestingly this rate constant for polymerization differs markedly from that determined using radiation techniques (radiation results were higher by a factor of 50). From our subsequent work doing this program, we now ascribe this remarkable difference to solvent effects. Indeed we studied the radiation-induced cationic polymerization of isopropyl vinyl ether (and also ethyl vinyl ether) in a variety of solvents and found the values to vary widely with the nature of the solvent. In particular, we found that a good linear relationship exists between the logarithms of the rate constants and the reciprocals of the dielectric constants. The lowest rates were those of the highest dielectric constant solvents.

The work on solvent effects led to other interesting findings. It was found that the rate of polymerization in the bulk and in a solvent such as benzene can be drastically altered by trace quantities of certain additives such as methylene chloride. The addition of a drop of methylene chloride in the bulk polymerization and when diluted with benzene yields rates of polymerization which are virtually identical to the rates of polymerization obtained in solutions of methylene chloride. We concluded that there is little or no solvation of the propagating species by the monomer. When even small quantities of methylene chloride are present, the results indicate that the methylene chloride molecules solvate the free ions and not the monomer. Further, our results indicate that in certain circumstances there could be a self-solvation of the propagating cations by their own chains. Finally, we have a paper that is now being prepared for publication which addresses the question of the stereochemistry of polyvinyl ethers produced by radiation induced cationic polymerization versus that for those derived by chemical initiation. The necessary NMR work is ongoing at the University of Paris.

The radiation chemistry work on polyphosphazenes has been a cooperative effort with scientists at AMRC. The work has progressed slowly due to complications. Specifically, the broad and sometimes bimodal nature of the molecular weight distributions of these polymers has necessitated a more extensive treatment of the data than the normally used sol gel analysis techniques. At this

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point, one paper on the radiochemical behavior of some poly (aryloxy phosphazenes) is being prepared for publication and a much more comprehensive manuscript is in the planning stages.

In summary, fourteen papers have been published during this 7-year period and two other manuscripts have been submitted for publication. It is likely that two other publications will eventually result from this project.

RESEARCH STAFF SUPPORTED

Postdoctoral Research Associates:

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H. Kubota
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J. A. Young

Graduate Students:

J. M. Rooney (Ph.D. awarded 1975)
M. Ma (Ph.D. awarded 1978)
W. C. Hsieh (Ph.D. awarded 1981)

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